Electrocatalytic Evolution of Oxygen Gas at Cobalt Oxide Nanoparticles Modified Electrodes

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1. Introduction :

The oxygen evolution reaction (OER) attracts a reasonable deal of attention as a consequence of its importance in a wide range of industrial applications such as water electrolysis, and energy conversion and storage devices. Metal oxide-based anodes, particularly those of nickel and cobalt, have long been used to catalyze the OER in alkaline electrolyzers due to their remarkable stability and activity [1-11]. Optimization of the operating experimental conditions (i.e., solution pH and loading level of nano-CoOx) has been achieved to maximize the electrocatalytic activity of nano-CoO*x* modified electrodes. The low cost as well as the marked stability of the thus-modified electrodes make them promising candidates in industrial water electrolysis process.

2. Material characterization:

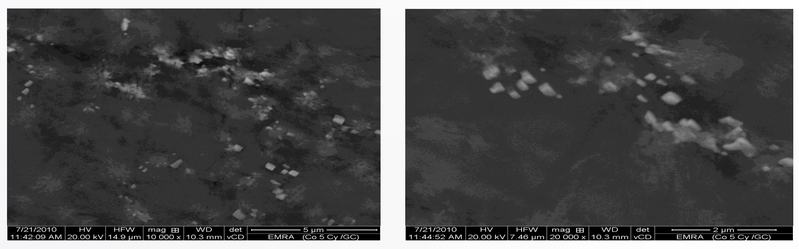
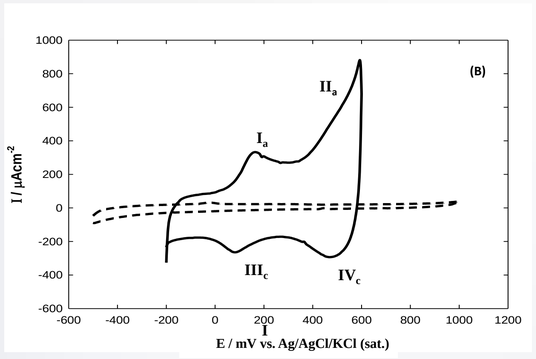


Fig. 1(A) FE-SEM micrographs of the electrodeposited CoO*x* on GC substrate. Note that CoOx is electrodeposited as described in the experimental section by employing 5 potential cycles in the range between 1.2 to -1.1 V vs. Ag/AgCl/KCl(sat) at a scan rate of 100 mV/s in PBS (pH 7.0) containing 1 mM $CoCl_2$.

2. Electrochemical characterization:



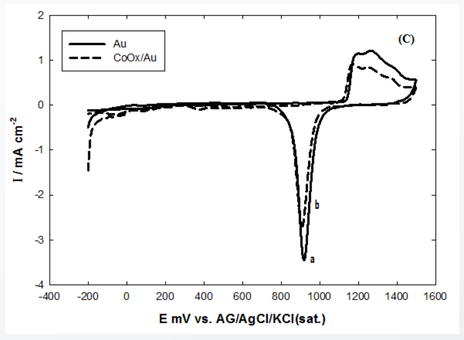


Fig. 1 (B) CV response of the bare (dashed curve) and nano-CoOx modified (solid curve) GC electrodes in 0.5 M KOH.

Fig. 1 (C) CV response obtained in 0.5 M H_2SO_4 at Au electrode modified with nano-CoO*x* (dashed curve) and the unmodified Au electrode (solid curve). Note that CoOx is electrodeposited as described in the caption of Fig. 1A.

3. Electrocatalytic activity and Effect of pH:

I / mA cm^{-2}	η_{O2} / mV		
	CoOx/GC	CoOx/Au	CoOx/Pt
5	456	423	459
10	483	453	567
15	500	468	580
20	517	487	610
25	530	496	643
30	542	506	677

Table 1 Oxygen evolution overpotential at nano-CoO*x* modified GC, Au and Pt electrodes in 0.5 M KOH at different current densities.

pH	ΔE_{10} / mV		
	CoOx/GC	CoOx/Au	CoOx/Pt
14	815	655	505
11	385	560	225
9	365	510	225
7	105	380	95
4	100	10	10
2	100	10	10

Table 2 Variation of ΔE_{10} of the OER obtained at nano-CoO*x* modified GC, Au and Pt electrodes with pH of the solution.

3. Effect of substrate:

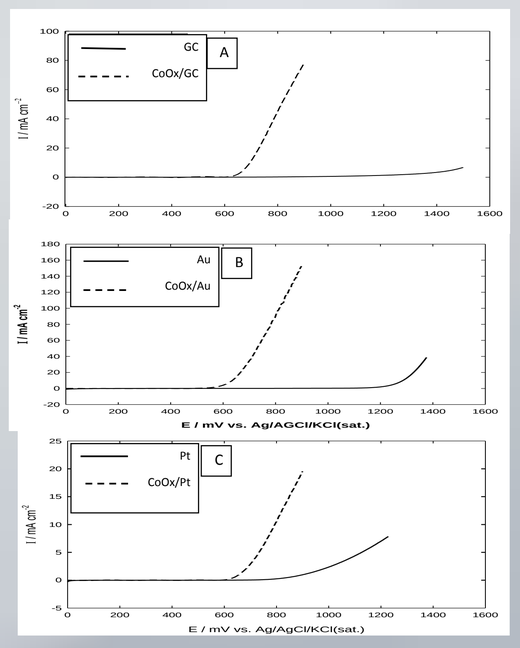


Fig. 2 (A-C) LSV response for the OER in 0.5 M KOH at the unmodified (solid curves) and the nano-CoO*x* (dashed curves) modified **(A)** GC, **(B)** Au and **(C)** Pt electrodes at potential scan rate of 20 mV s^{-1}.

3. Nano-CoOx vs. Nano-NiOx

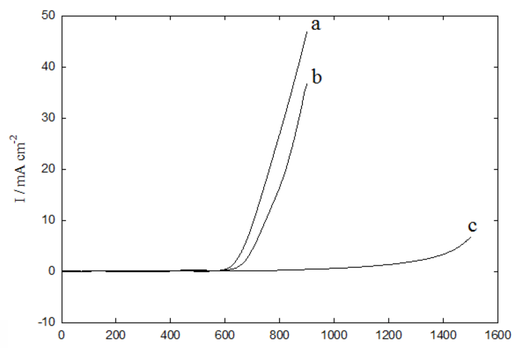


Fig. 2 (D) LSV response for the OER obtained in 0.5 M KOH at (a) nano-CoO*x* , (b) nano-NiO*x* modified GC electrodes, and (c) unmodified GC electrode at potential scan rate of 20 mV s^{-1}.

5. Loading level

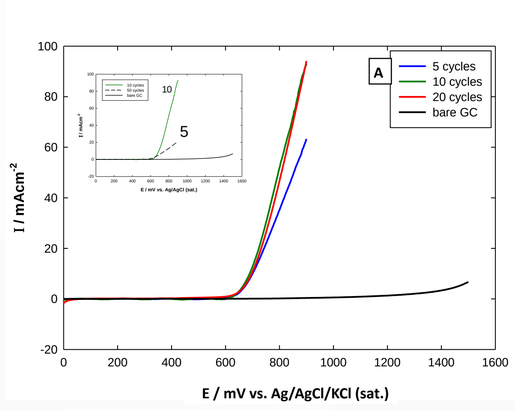


Fig. 3 LSV response for the OER in 0.5M KOH at GC electrode modified with electrodeposited nano-CoOx with different potential cycles (5, 10, 20 and 50 pot. cycles) at a potential scan rate of 20 mV s^{-1}. The numbers refer to the potential cycles employed for the deposition of nano-CoO*x*.

2. Ageing and stability

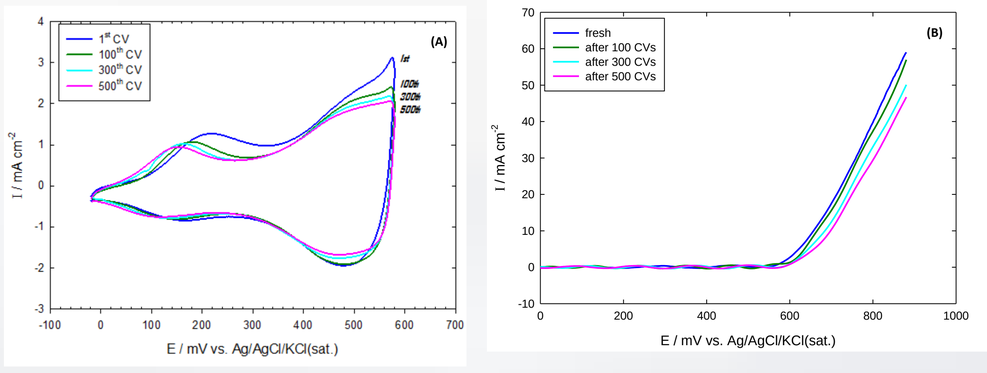


Fig. 4 (A) CV responses at the nano-CoO*x* modified GC electrode in 0.5 M KOH after ageing for several potential cycles (1st, 100, 300 and 500 potential cycles).

Fig. 4 (B) The LSV response of the OER in 0.5 M KOH at the nano-CoO*x* modified GC after ageing in 0.5 M KOH for several potential cycles up to 500 CVs (see **Fig. 4 (A)**).

7. Conclusions:

Cheap, efficient, and stable nano-CoO*x*-based anodes are proposed as electrocatalysts for the OER. This electrocatalyst was fabricated by a potential cycling method which resulted in deposition of CoO*x* in the form nanometer-scale aggregates. The maximum electrocatalytic activity towards the OER was obtained in alkaline media (pH > 9). The electrocatalytic activity of the modified electrodes increased with the number of potential cycles employed for the CoO*x* deposition till a certain loading beyond which an adverse effect is observed. The thus-fabricated nano-CoO*x* modified electrodes exhibited a good stability and durability as revealed from the aging experiments.

References:

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